10/642,367

PTO 07-6659

CC = JP
19910509
Kokai
03109358

PRODUCTION METHOD FOR DIALKYL CARBONATES
[Jiarukirukaabonetono Seizohoho]

Haruyuki Minora

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. SEPTEMBER 2007
TRANSLATED BY: THE MCELROY TRANSLATION COMPANY

PUBLICATION COUNTRY	(19):	JP
DOCUMENT NUMBER	(11):	03109358
DOCUMENT KIND	(12):	Kokai
PUBLICATION DATE	(43):	19910509
APPLICATION NUMBER	(21):	1246330
APPLICATION DATE	(22):	19890925
INTERNATIONAL CLASSIFICATION[5]	(51):	C 07 C 69/96
		69/06
INVENTOR	(72):	Haruyuki Minora
APPLICANT	(71):	Asahi Chemical Industry Co., Ltd.
TITLE	(54):	PRODUCTION METHOD FOR DIALKYL CARBONATES
FOREIGN TITLE	[54A]:	Jiarukirukaabonetono Seizohoho

Claim

A production method for dialkyl carbonates, characterized in that in the method for producing dialkyl carbonates from raw materials containing cyclic carbonates and alcohols in the presence of a solid basic anion exchange resin containing quaternary ammonium group or tertiary amine group as functional group and carbonate radical and/or bicarbonate radical, raw materials with water concentration of 160 ppm or less are used.

Detailed explanation of the invention

Industrial application field of the invention

The present invention relates to a production method for dialkyl carbonates.

More specifically, the present invention relates to a production method for dialkyl carbonates, which is characterized in that raw materials containing cyclic carbonates and alcohols with water concentration of 160 ppm or less are reacted at relatively low temperatures in the presence of a solid basic anion exchange resin.

Prior art

Homogeneous catalysts have been used mainly in methods for producing dialkyl carbonates by reacting cyclic carbonates with alcohols in the presence of catalysts, such as a method of utilizing tertiary aliphatic amines as the catalysts, a method of utilizing alkali metal or alkaline earth metal compounds as the catalysts, a method of utilizing thallium compounds as the catalysts, a method of utilizing tin alkoxides as the catalysts, a method of utilizing composite catalysts from Lewis acid and nitrogen-containing organic bases, a method of utilizing quaternary phosphonium salts as the catalysts, etc.

In this case, there is the problem of difficulty in separating of catalysts and reaction products.

On the other hand, as methods of utilizing heterogeneous catalysts where the separation of catalysts and reaction products is easy, there are methods utilizing basic exchange resins containing tertiary aliphatic amine groups (Japanese Patent No. Sho 59[1984]-28542), utilizing strong-basic exchange resins containing quaternary ammonium groups (Kokai Patent No. Sho 63[1988]-238043), a method of utilizing basic or acidic exchange resins sand silicates containing alkali and alkaline earth metals (Kokai Patent No. Sho 64[1989]-31737), and utilizing silica-titania solid catalysts (Japanese Patent No. Sho 61[1986]-5467), etc.

Problems to be solved by the invention

The methods for producing dialkyl carbonates by reacting cyclic carbonates with alcohols using publicly known heterogeneous catalysts require relatively high reaction temperatures due to catalyst activity, and this causes deterioration of exchange resins having low heat-resisting temperature. Further, those have the problem that side reactions such as dehydration condensation of glycol during reaction, etc., occur, so that the selectivity is lowered.

Means to solve the problems

The present inventor et al. had studied assiduously the method for producing dialkyl carbonates from cyclic carbonates and alcohols and, as a result, it was found that when raw materials with water concentration of 160 ppm and less and solid basic anion exchange resin catalysts are used, dialkyl carbonates, which are stable for a long time, can be produced at extremely high yield, even in a low temperature range.

Namely, the present invention provides a production method for dialkyl carbonates, characterized in that dialkyl carbonates are produced by reacting raw materials containing cyclic carbonates and alcohols with water concentration of 160 ppm or less in the presence of a solid basic anion exchange containing quaternary ammonium group or tertiary amine group as functional group and carbonate radical and/or bicarbonate radical.

As cyclic carbonates to be used in the present invention, for instance, alkylene carbonates, such as ethylene carbonate, propylene carbonate, etc., 1,3-dioxycyclohexa-2-one, 1,3-dioxacyclohepta-2-one, etc., may be exemplified, but ethylene carbon and propylene carbonate are preferably used since those are easily obtained.

Further, as alcohols, for instance, aliphatic alcohols, such as methyl alcohol, ethyl alcohol, propyl alcohol, 1-methyl ethyl alcohol, etc., and monohydric alcohols with carbon number of 1-12, such as alicyclic alcohol, e.g., cyclohexanol, etc., can be used.

Catalysts to be used in the present invention are strongly basic anion exchange resins having quaternary ammonium groups as a functional group and weakly basic anion exchange resins having a tertiary amine group as a functional group, and those have carbonate radical and/or bicarbonate radical. Further, as resin base body, styrene system gel type and macroreticular type (MR type) can be used, but MR type is preferred since the resistance to organic solvents is high.

Commercial products can be used as solid strongly basic anion exchange resins and solid weakly basic anion exchange resins having quaternary ammonium group or tertiary amine group as functional group. In this case, it is preferred to carry out ion exchange of those resins beforehand as pretreatment, and to dehydrate and use those as catalysts.

The aforementioned anion exchange resins are used generally in the form of fine powder or spherical particles having average particle diameter of 0.2-10 mm.

As the reaction mode, methods used generally such as fluidized bed type, fixed bed type or agitation type, etc., can be used. Further, it may be circulation type or batch type, and the separation of the reaction solutions and catalysts can be carried out easily.

The reaction temperature for executing the present invention is generally 0-120°C, but a relatively low temperature of 0-45°C is preferable for stability of catalysts and inhibition of byproducts. Further preferably, it is 15-40°C even at which a sufficient yield is obtained.

The reaction time varies with type and composition ratio of cyclic carbonates and alcohols as raw materials and also reaction temperature, but in the case of, for instance, circulation reaction, it is, in terms of liquid space velocity (LHSV) to total feed, is generally about 0.05-40 h^{-1}, preferably 0.1-20 h^{-1}, further preferably 0.2-10 h^{-1}. Further, in the case of batch reaction, it is generally 0.05-60 h^{-1}, preferably 0.1-40 h^{-1}, and further preferably 0.2-20 h^{-1}.

The quantity ratio of cyclic carbonates to alcohols in raw materials can be used in a wide range. When the molar ratio of alcohols to cyclic carbonates is too high, however, the quantity of alcohols to be recovered becomes large so that it is not practical. Further, when the molar ratio is too low, the recovering amount increases and it is also not practical since the conversion of cyclic carbonates decreases.

Therefore, the molar ratio of alcohols to cyclic carbonates in raw materials is used at generally 0.05-100, preferably 0.1-40, and further preferably 0.2-20.

In the present invention, the water content in raw materials shows a big influence on the yield of dialkyl carbonates, and this influence is high especially under low-temperature conditions. When the water content exceeds 200 ppm the catalyst efficiency lowers notably so that the yield of dialkyl carbonate lowers.

Therefore, it is necessary to make the water concentration in raw materials 160 ppm or less, preferably 130 ppm or less, and further preferably 100 ppm or less.

Raw materials may contain, for instance, recycle reaction intermediates and solvents, etc., if desired beside cyclic carbonates and alcohols, and it is necessary that the water content be in the aforementioned concentration range with respect to total feed solution being fed to the reaction system.

Application examples

Hereinafter, the present invention is explained in detail by application examples, but the present invention is not limited to these application examples only.

Furthermore, the conversion, selectivity and yield shown in application examples were calculated by the following equations.

Conversion (%)

= [feed quantity of cyclic carbonates (mol) – unreacted cyclic carbonates (mol)] x 100/[feed quantity of cyclic carbonates (mol)]

Selectivity (%)

= [production quantity of dialkyl carbonates (mol)] x 100/[feed quantity of cyclic carbonates (mol) – unreacted cyclic carbonates (mol)]

Further, in this reaction, monoalkyl-substituted carbonate was produced as reaction intermediate, but this was considered cyclic carbonate by raw material equivalence.

Application Example 1

(Preparation of catalyst)

Dowex MSA-1 (styrene system strong-basic anion exchange resin ((1 type), anion type Cl^-, Dow Chemical Co., Ltd.) was pretreated by the following method to include carbonate radical.

(1) Dowex MSA-1 250 mL was stirred in 1N NaOH aqueous solution 500 mL for 1 hour, filtered and washed with 2000 mL water.

(2) After repeating the procedure of (1), it was washed until its pH reached 7.

(3) It was again stirred in 1N Na_2CO_3 aqueous solution 500 mL for 1 h, filtered and washed with 2000 mL water.

(4) After repeating twice the procedure of (3), it was washed until its pH reached 7.

(5) After completing the procedures of (1)-(4), the resin was dehydrated by repeating the procedure of putting into 500 mL dehydrated methanol, stirring for 10 minutes, and decanting. Then, the resin was preserved in dehydrated methanol to obtain catalyst A.

(Reaction)

The catalyst A was packed into a tubular reactor (outer diameter 12.7 mm, inner volume 20 mL) and after immersing it in oil bath, methanol was fed at 20°C and 1 kg/cm^2. Then, an ethylene carbonate-methanol mixed raw material (methanol/ethylene carbonate molar ratio = 2) with water concentration of 100 ppm was fed at a flow rate of 40 mL/h (LHSV=2). When the reaction system reached steady state the reaction solution was analyzed by a temperature-raising gas chromatograph equipped with PEG20M glass column 2m (the column temperature was raised from 60°C to 220°C at 10°C/min, detection tube FID).

As its result, the conversion of ethylene carbonate was 45%; the selectivity of dimethyl carbonate was 99% and higher; dimethyl carbonate showed almost equilibrium yield. Further, the formation of CO_2 as a reaction byproduct was not found.

Application Example 2

The reaction was carried out by the same method as in Application Example 1 using same catalyst A and raw material with water concentration of 100 ppm, except that the feed quantity of the raw material was changed to 100 mL/h (LHSV = 5). As is seen in the result shown in Table 1, dimethyl carbonate was obtained at extremely high yield, and the formation of CO_2 as a reaction byproduct was not found.

Application Example 3

The reaction was carried out by the same method as in Application Example 1 using same catalyst A and raw material with water concentration of 100 ppm, except that the reaction temperature was set at 40°C, and the reaction pressure was 5 kg/cm^2. The result is shown in Table 1. Further, the formation of CO_2 as a reaction byproduct was not found.

Application Example 4

The reaction was carried out by the same method as in Application Example 1 using same catalyst A and raw material with water concentration of 100 ppm, except that the reaction temperature was set at 60°C, and the reaction pressure was 5 kg/cm^2. The result is shown in Table 1. Further, a very small amount of CO_2 as a reaction byproduct was detected.

Application Example 5

The reaction was carried out by the same method as in Application Example 1 using same catalyst A and raw material with water concentration of 100 ppm, except that the reaction temperature was set at 90°C, and the reaction pressure was 5 kg/cm^2. The result is shown in Table 1. Further, CO_2 as a reaction byproduct was produced at an amount of 0.08 mole based on the raw material ethylene carbonate.

TABLE 1

	Reaction temperature (°C)	Reaction pressure (kg/cm^2)	LHSV (h^{-1})	Ethylene carbonate conversion (%)	Dimethyl carbonate selectivity (%)
Application Example 1	20	1	2	45	>99
Application Example 2	20	1	5	39	>99
Application Example 3	40	5	2	43	>99
Application Example 4	60	5	2	41	>99
Application Example 5	80	5	2	39	>99

As it is seen in Application Examples 1-5, the conversion of ethylene carbonate shows high value as the reaction temperature lowers.

Application Example 6

The reaction was carried out by the same method as in Application Example 1 using same catalyst A, except that the water concentration of ethylene carbonate-methanol mixed raw material was set at 150 ppm. The result is shown in Table 2.

Comparative Example 1

The reaction was carried out by the same method as in application example 1using same catalyst A, except that the water concentration of ethylene carbonate-methanol mixed raw material was set at 200 ppm. The result is shown in Table 2.

	Water concentration (ppm)	Ethylene carbonate conversion (%)	Dimethyl carbonate selectivity (%)
Application Example 6	150	40	>99
Comparative Example 1	200	5	>99

Comparative Example 2

(Preparation of catalyst)

Catalyst B having chlorine radical was obtained by the same manner as in Application Example 1 except that 1N HCl, instead of 1N Na_2CO_3 aqueous solution, was used.

(Reaction)

The reaction was carried out by the same method as in application example 1using same raw material with water concentration of 100 ppm, except that the catalyst B was used. As its result, the formation of dimethyl carbonate was not found.

Application Example 7

Catalyst adjustment of Amberlyst A-21 (tertiary aliphatic amine type (freebase type) weak-basic anion exchange resin, Roam & Haas Co.) was carried out by the same method as in Application Example 1 to obtain catalyst C having carbonate radical.

(Reaction)

The reaction was carried out by the same method as in application example 1using same raw material with water concentration of 100 ppm, except that the catalyst C was used. As its result, the conversion of ethylene carbonate was 27%, and the selectivity of dimethyl carbonate was 99% and higher.

Comparative Example 3

The reaction was carried out by the same method as in Application Example 8 [sic] using the same Amberlyst A-21 catalyst except that the water concentration of ethylene carbonate-methanol mixed raw material was set at 200 ppm. As its result, the conversion of ethylene carbonate was 2%, and the selectivity of dimethyl carbonate was 99% and higher.

Application Example 8

The same reaction as in Application Example 1 using ethylene carbonate-methanol mixed raw material with water concentration of 100 ppm was carried out continuously for 1000 h. Its results are shown in Table 3.

TABLE 3

Reaction time (h)	Ethylene carbonate conversion (%)	Diethyl carbonate selectivity
5	45	>99
100	44	>99
500	45	>99
1000	45	>99

Application Example 9

Catalyst A 50 mL and ethylene carbonate-methanol mixed raw material (methanol/ethylene carbonate molar ratio = 2, water concentration 100 ppm) 230 g were packed into a 500 mL autoclave, and the reaction was carried out by conducting N_2 purging several times and initiating stirring at 20°C. After 60 min, the reaction solution was analyzed. The conversion of ethylene carbonate was 45%, and the selectivity of dimethyl carbonate was 99% and higher.

Application Example 10

The reaction was carried out by the same method as in Application Example 1 using the same catalyst A with raw material water concentration of 100 ppm, except that the reaction temperature was changed from 20°C to 40°C and propylene carbonate (methanol/propylene carbonate molar ratio = 2) was used instead of ethylene carbonate. As its result; the conversion of ethylene carbonate was 40%, and the selectivity of dimethyl carbonate was 99%.

Application Example 11

The reaction was carried out by the same method as in Application Example 1 using the same catalyst A with raw material water concentration of 100 ppm, except that the reaction temperature was changed from 20°C to 40°C and ethanol (ethanol/propylene carbonate molar ratio = 2), instead of methanol, was used. As its result, the conversion of ethylene carbonate was 41%, and the selectivity of dimethyl carbonate was 99%.

Effect of the invention

According to the present invention, dialkyl carbonates can be obtained at high yield and high selectivity under gentle reaction conditions using cyclic carbonates and alcohols as raw materials.

In addition, dialkyl carbonates can be produced stably for a long time since there is almost no degradation of catalysts, and its industrial advantage is extremely great.